

PATENT SPECIFICATION

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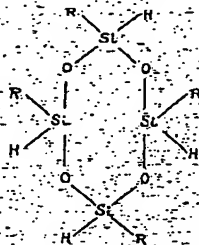
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COMPLETE SPECIFICATION

Improvements in and relating to Polysiloxanes

We, THE BRITISH THOMSON-HOUSTON COMPANY LIMITED, a British Company having its registered office at Crown House, Aldwych, London, W.C.2, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to new and useful chemical compounds and more particularly is concerned with compounds known as polysiloxanes. Specifically the invention relates to new cyclopoly-siloxanes corresponding to the general formula $(RSiHO)_n$, where R represents a lower alkyl radical (e.g., methyl, ethyl, propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl) and *n* represents 4, 5 or 6, and to methods of preparing such cyclopoly-siloxanes. Cyclopoly-siloxanes corresponding to, for example, the general formula $(RSiHO)_n$, where R represents a lower alkyl radical, also may be represented by the formula



In a similar manner structural formulas for cyclopoly-siloxanes corresponding to the general formulas $(RSiHO)_n$ and $(RSiHO)_n$, that is cyclopoly-siloxanes containing 5 or 6 Si atoms linked with oxygen atoms in a ring structure, may be written.

It was known prior to the invention that cyclic compounds having the formula $[(CH_3)_2SiO]_n$, where *n* is an in-

teger which is at least 3 and not more than 10 could be prepared, for example by heating the higher boiling polymers of dimethyl silicone having the formula $[(CH_3)_2SiO]_n$, where *n* is an integer greater than 10, at an elevated temperature (above 200° C.) in a non-oxidizing atmosphere. Such cyclic silicon compounds are more fully described in British Specification No. 686,188. The compounds of the present invention, more particularly cyclopoly-siloxanes corresponding to the general formula $(CH_3SiHO)_n$, where *n* represents 4, 5 or 6, differ from those disclosed in the aforementioned specification, in that, instead of two methyl groups being attached directly to each nuclear Si atom, there are attached thereto one methyl group and one hydrogen atom.

The cyclopoly-siloxanes of this invention are especially valuable as intermediates in the preparation of other organo-silicon compounds for instance linear polysiloxanes of the kind disclosed in copending application No. 7700/47 (Serial No. 632,954). These cyclic compounds, specifically the symmetrical polymethylcyclopoly-siloxanes, also are useful in making other new organo-polysiloxanes, more particularly oils of improved viscosity-temperature coefficient.

The cyclopoly-siloxanes with which this invention is concerned may be prepared by causing a halogenosilane corresponding to the general formula $RSiHX_2$, where R represents a lower alkyl radical and X represents chlorine or bromine, to react with water (i.e. to be hydrolyzed) whereby there are obtained cyclopoly-siloxanes corresponding to the general formula $(RSiHO)_n$, where R has the meaning above given and *n* represents 4, 5 or 6 and isolating the said cyclopoly-siloxanes, e.g. by distillation, from the resulting reaction mass. The halogenosilanes used in practising this method

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(CH_3SiHO)_n, where n represents a large whole number (possibly 15 to 30 or more) is formed. The greater reactivity of the siloxane linkages in the compounds of the invention, e.g., the methyl derivatives, as compared with the corresponding cyclic polymers of dimethyl silicone, is further shown by the fact that they polymerize to semisolid or solid bodies on standing for a prolonged period, e.g., 9 to 12 months or more, at room temperature while exposed to air and light. The enhanced reactivity of the siloxane linkages in the new compounds may be due to diminution of the steric hindrance of the groups attached to silicon since the hydrogen atom is smaller than a methyl group.

In order that those skilled in the art better may understand how the present invention may be carried into effect, the following examples are given by way of illustration and not by way of limitation:

EXAMPLE 1.

Four moles (460 g.) of methyl dichlorosilane, b.p. 41.3° C. (760 mm.), 61.4% Cl, was added with vigorous stirring to a mixture of 1 liter of diethyl ether containing a small amount of benzene, and 2 kilograms of cracked ice over a half-hour period. The temperature of the hydrolyzing mixture dropped from 0° C. to minus 10° C., but rose finally to plus 7° C. After stirring for an additional

half hour the aqueous layer was separated and the organic phase washed (three times with water until it was neutral to methyl orange. After removal of the ether and the small amount of benzene, the product was fractionated by distillation first at atmospheric pressure and then under reduced pressure as the temperature of distillation was increased. By this distillation there was obtained, by weight, about 36% of 1, 3, 5, 7-tetramethylcyclotetrasiloxane, b.p. 134.5-134.9° C. (755 mm.); about 17% of 1, 3, 5, 7, 9-pentamethylcyclopentasiloxane, b.p. 168.6-168.9° C. (755 mm.); and about 4% of impure 1, 3, 5, 7, 9, 11-hexamethylcyclohexasiloxane, b.p. 92.6-93° C. (21 mm.) together with forerunners and intermediate fractions amounting to about 14% and a residue of about 28%. No effort was made to identify the composition of this residue. However, it is possible that it comprised a mixture of 1, 3, 5, 7, 9, 11, 13-heptamethylcycloheptasiloxane, 1, 3, 5, 7, 9, 11, 13, 15-octamethylcyclooctasiloxane, 1, 3, 5, 7, 9, 11, 13, 15, 17-nonamethylcyclononasiloxane and higher homologues, as well as other compounds. The impure hexamethyl derivative was refractionated to obtain a purer material having a boiling point of 76-77° C. at 10.2 mm. pressure. Other data on the characteristics of the tetramer, pentamer and hexamer (purified material) are given in the following table:

TABLE I.

	n_D^{20}	d_4^{20} (vac.)	R_D	m.p. (° C.)	Mol. Wt. Calculated	Found*	%H (attached to Si)** Found
Tetramer	1.3870	0.9912	0.2375	-69±3	240.4	239, 241, 244	1.64, 1.64
Pentamer	1.3912	0.9983	0.2381	-108±3	300.5	298, 297, 297	1.65
Hexamer	1.3944	1.006	0.2380	-79±2	360.6	360	1.67

* Cryoscopic in cyclohexane; maximum concentration of solute in weight per cent.: tetramer, 0.56; pentamer, 0.72; hexamer, 0.78.

** Theoretical for CH_3SiHO , 1.68.

In separating the above-described cyclopolyxiloxanes by distillation from the hydrolyzate, the distillation took place under non-oxidizing or substantially non-oxidizing conditions since the forerunners swept the distillation apparatus free or substantially free from

air. In this way oxidation of the hydrolyzate and of the compounds distilled therefrom during distillation was avoided or minimized.

In a manner similar to that described above with particular reference to the preparation of 1, 3, 5, 7-tetramethylcyclo-

dichlorosilane with a quantity of water cyclopentasiloxane and 1,3,5,7,9,11-hexamethylcyclohexasiloxane, other lower alkyl cyclopolsiloxanes of similar structure may be obtained by hydrolyzing the corresponding lower alkyl dichloro or dibromo silanes, examples of which have been given hereinbefore, and isolating the resulting cyclopolsiloxanes from the oily hydrolyzate.

In a manner similar to that hereinbefore described with particular reference to the preparation of 1,3,5,7-tetramethylcyclotetrasiloxane, 1,3,5,7,9-pentamethylcyclopentasiloxane and 1,3,5,7,9,11-hexamethylcyclohexasiloxane, other cyclopolsiloxanes embraced by the general formula $(RSiHO)_n$, where R represents a lower alkyl radical and n represents 4, 5 or 6, may be prepared and thereafter polymerized. Examples of such compounds and polymers thereof are:

- 1,3,5,7-tetraethylcyclotetrasiloxane
- 1,3,5,7-tetrapropylcyclotetrasiloxane
- 1,3,5,7-tetraisopropylcyclotetrasiloxane
- 1,3,5,7-tetra-n-butylcyclotetrasiloxane
- 1,3,5,7-tetra-sec-butylcyclotetrasiloxane
- 1,3,5,7-tetra-iso-butylcyclotetrasiloxane
- 1,3,5,7,9-pentaethylcyclopentasiloxane
- 1,3,5,7,9-pentapropylcyclopentasiloxane
- 1,3,5,7,9-pentaisopropylcyclopentasiloxane
- 1,3,5,7,9-penta-n-butylcyclopentasiloxane
- 1,3,5,7,9-pentaisobutylcyclopentasiloxane
- 1,3,5,7,9-penta-sec-butylcyclopentasiloxane
- 1,3,5,7,9-penta-iso-butylcyclopentasiloxane
- 1,3,5,7,9,11-hexaethylcyclohexasiloxane
- 1,3,5,7,9,11-hexapropylcyclohexasiloxane
- 1,3,5,7,9,11-hexaisopropylcyclohexasiloxane
- 1,3,5,7,9,11-hexa-n-butylcyclohexasiloxane
- 1,3,5,7,9,11-hexaisobutylcyclohexasiloxane
- 1,3,5,7,9,11-hexa-sec-butylcyclohexasiloxane
- 1,3,5,7,9,11-hexa-iso-butylcyclohexasiloxane
- siloxane and polymers thereof.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:

1. The method of preparing cyclopolsiloxanes which consists in slowly adding a lower alkyl dichloro silane with vigorous stirring to a cold mixture of an inert organic diluent and water stirring the reaction mass for a further period after the addition of all of the lower alkyl dichloro silane, and separating cyclopolsiloxanes corresponding to the formulas $(RSiHO)_4$, $(RSiHO)_5$ and $(RSiHO)_6$ from the organic phase containing the same.

2. The method of preparing cyclopolsiloxanes which consists in slowly adding methyldichlorosilane with vigorous stirring to a mixture of diethyl ether and ice, stirring the reaction mass for a further period after the addition of all of the methyldichlorosilane, washing the organic phase comprising diethyl ether with water until it is substantially neutral, and separating by distillation from the washed organic phase cyclopolsiloxanes represented by the formulas $(CH_3SiOH)_4$, $(CH_3SiOH)_5$ and $(CH_3SiOH)_6$.

3. A cyclopolsiloxane prepared by the method claimed in Claim 1 or 2 corresponding to the general formula $(RSiHO)_n$, where R represents a lower alkyl radical and n represents 4, 5 or 6.

4. A cyclopolsiloxane prepared by the method claimed in claim 1, 2 or 3 corresponding to the general formula $(CH_3SiOH)_n$, where n represents 4, 5 or 6.

5. A method according to Claim 1 or 2, in which the corresponding bromosilane is used instead of the chlorosilane.

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